

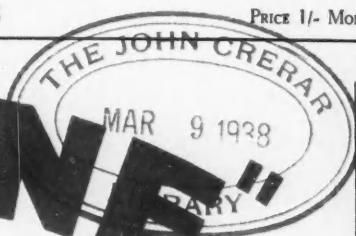
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CEMENT AND LIME  
MANUFACTURE

Vol. XI. No. 1

JANUARY 1938

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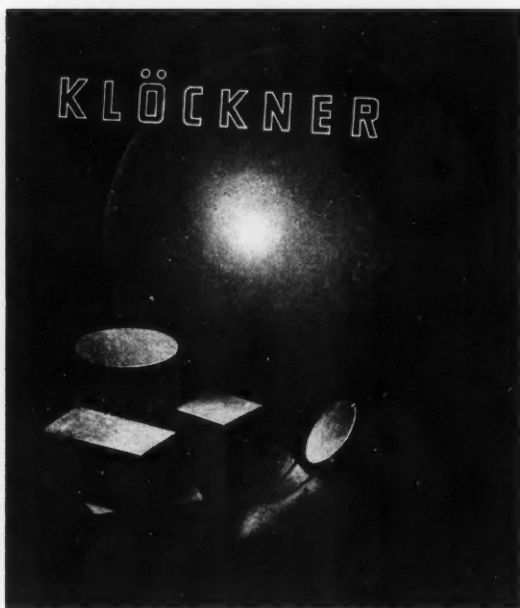
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VOLUME XI. NUMBER 1

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## Proportioning and Chemical Control of Raw Mixes.

PORTLAND cement may be made from a number of materials, of which the following are examples :

- (1) Limestone and clay or shale.
- (2) Cement rock and limestone.
- (3) Chalk and clay or shale.
- (4) Marl and clay or shale.
- (5) Alkali waste and clay or shale.
- (6) Slag and limestone.

The preparation of a homogeneous raw mixture of correctly proportioned lime content and of good quality clinker depends to a very large extent on the raw materials available. Thus marls with a composition near to that required in a cement raw mixture have a great advantage over materials of widely different composition. The following are among the major points to be observed in selecting raw materials.

(1) Coarse sand, traces of lead or zinc or their compounds, excess magnesia, alkalis, sulphides, sulphates, and phosphates should be avoided.

(2) In a limestone the calcium carbonate content must reach a minimum of 75 per cent. Poor limestone may be enriched by adding a proportion of purer stone to raise the percentage of calcium carbonate. If the stone contains more than 2 per cent.  $MgO$  it is unsuitable for making Portland cement to meet the requirements of standard specifications unless the clay or shale is very low in this constituent. The amount of iron oxide should not be so high as to cause the  $Fe_2O_3$  in the clinker to exceed 6.0 per cent.

(3) In every case it is better to consider the calcareous and argillaceous materials together so that in the mixture of the two, calculated on a lime saturation basis, the  $SiO_2/R_2O_3$  ratio, the  $Al_2O_3/Fe_2O_3$  ratio, and the  $MgO$ ,  $Al_2O_3$  and  $Fe_2O_3$  contents are satisfactory.

(4) Clay containing an appreciable amount of coarse sand must either be rejected or finely ground.

The theoretical lime saturation content of a cement mix is given by the following formula\*:

$$\text{CaO} = 2.8 \text{ SiO}_2 + 1.18 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3.$$

The following is a practical example of the use of the formula, assuming the analysis of the raw materials is as follows:

	Limestone (per cent.).	Shale (per cent.).
Silica .. .. .	1.22	56.38
Alumina .. .. .	0.34	20.00
Iron oxide .. .. .	0.44	5.52
Lime .. .. .	54.46	0.74
Magnesia .. .. .	0.48	2.33
Sulphur trioxide .. .. .	0.03	1.64
Loss on ignition .. .. .	42.95	12.00

In the limestone,

$$\text{SiO}_2 \times 2.8 = 3.416$$

$$\text{Al}_2\text{O}_3 \times 1.18 = 0.401$$

$$\text{Fe}_2\text{O}_3 \times 0.65 = 0.286$$

---


$$4.103$$

$$\text{CaO} \times 1.00 = 54.46. \quad 54.46 - 4.103 = 50.357.$$

In the shale,

$$\text{SiO}_2 \times 2.8 = 157.864$$

$$\text{Al}_2\text{O}_3 \times 1.18 = 23.600$$

$$\text{Fe}_2\text{O}_3 \times 0.65 = 3.588$$

---


$$185.052$$

$$\text{CaO} \times 1.00 = 0.740$$

---


$$184.312$$

Therefore the theoretical formula requires  $\frac{184.312}{50.357} = 3.66$  parts of limestone to be added to one part of shale.

In order to arrive at the practical proportions of limestone and shale, two opposing factors have to be considered: (1) To combine all the lime required by the proportions given necessitates a very fine homogeneous slurry perfectly burned. These conditions are rarely possible in commercial works practice, so that for this reason the tendency is to start with a somewhat lower ratio of limestone to shale than that given by the formula. (2) The ash of the coal used for burning will materially reduce the lime ratio of the theoretical mix, so the tendency here is to take a higher ratio of limestone to shale than is required by the formula.

Thus no hard and fast formula for proportioning can be laid down initially to suit all works and raw materials. The two factors mentioned should, however,

\* Lea and Parker (Building Research Technical Paper, No. 16, "The Quaternary System  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$ ").

more or less tend to cancel each other so that a start might be made with the proportions of limestone and shale given by the theoretical formula. The percentage composition of the slurry would therefore be :

	Per cent.
Silica .. .. .	13.06
Alumina .. .. .	4.55
Ferric oxide .. .. .	1.53
Lime .. .. .	42.94
Magnesia .. .. .	0.87
Sulphur trioxide .. .. .	0.38
Loss .. .. .	36.31

99.64

B.S.S. lime ratio = 2.92

Per cent.  $\text{SiO}_2$  = 2.14

Per cent.  $\text{Al}_2\text{O}_3$  = 3.00

Per cent.  $\text{Fe}_2\text{O}_3$  = 3.00

$$\text{B.S.S. lime ratio} = \frac{0.01786 (\text{per cent. CaO} - 0.7 \text{ per cent. SO}_3)}{0.01667 \text{ per cent. SiO}_2 + 0.0098 \text{ per cent. Al}_2\text{O}_3}$$

Due to admixture with coal ash, the B.S.S. lime ratio on the clinker will fall from 0.20 to 0.25 from the slurry value for this ratio, and will therefore, according to general practice, be between 2.72 and 2.67.

#### Control of Raw Mix.

If the amount of water, organic matter, and magnesia is fairly constant in the raw materials, and if the silica ratio of the raw materials does not show more than a very slight variation, then for a given B.S.S. lime ratio in the clinker there will be a constant value for the percentage of lime in the clinker and for the calcium carbonate in the slurry.

It follows that when the value of the ratio

Per cent. calcium carbonate in slurry : per cent. calcium oxide in clinker is known, all that is necessary for the control of the raw mix is the determination of the percentage of calcium carbonate in the slurry. In the best practice the proportion of lime in the clinker and the silica ratio of the clay will also be determined periodically as a check. In works where varying quantities of sand in the clay cannot be avoided it is essential to keep a check on the silica ratio of the clay if the clinker-lime-ratio is to be kept at all uniform. To attempt to deduce the calcium oxide content of the clinkered slurry from determinations of the calcium carbonate (by works routine methods) and loss on ignition of the slurry may be misleading, because the calcium carbonate value found varies with the method of determination according to the form and amount of magnesia or magnesium carbonate present. Some, all, or none of the magnesia may be found according to its amount and form and the method in which carbonate is determined. Thus in a high-magnesia slurry the "acid-alkali" method of calcium carbonate determination gives higher values for  $\text{CaCO}_3$  than does the gas-volume method of determination.



**Methods of Determination of Calcium Carbonate.**

Two methods are in general use for determining the calcium carbonate content, namely:

(1) The indirect gas method in which the carbonate of lime is decomposed by acid and the evolved carbon dioxide gas collected in a suitable apparatus and measured. Since the carbon dioxide is proportional to the calcium carbonate,

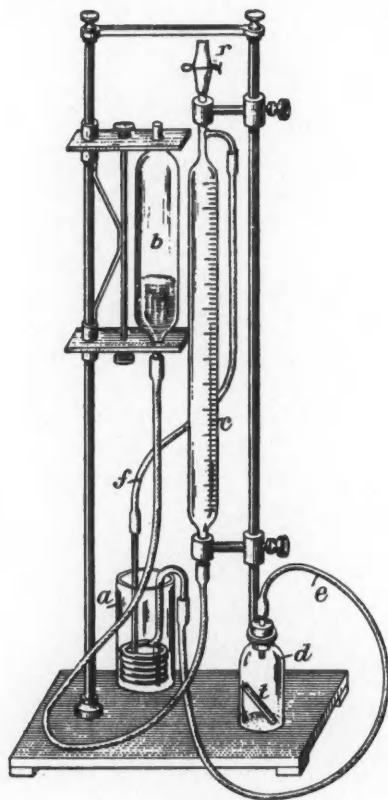


Fig. 1.

the percentage of carbonate can be calculated from the volume of carbon dioxide found. The instruments used in this method are known as calcimeters.

(2) The alkalimetric method in which the calcium carbonate is decomposed by a measured quantity of standard nitric or hydrochloric acid and the excess of acid determined by titration with standard alkali.

**DIETRICH-FRUHLING CALCIMETER.**—The apparatus (*Fig. 1*) consists of a 200 cc. graduated burette (*c*) connected at its lower end to a levelling tube (*b*)



by means of rubber pressure tubing. The top of the burette is closed by a piece of rubber tubing fitted with a pinch-cock (r). The decomposition flask (d), closed by a rubber stopper, is connected by rubber tubing (e) to a water-cooled spiral in the jacket (a); the tubing (f) connects the spiral and the burette. The graduated burette is vertically clamped, whilst the levelling tube can be moved up and down. To use the apparatus, raise the levelling tube and fill it with water so that the water level reads zero in the burette and a little above this level in the levelling tube. Note the temperature and barometric pressure, and from the table which follows find the weight of substance (previously dried at 105 deg. C.) to be used. Place the weighed substance into the decomposition flask, which must be dry and clean. Run 5 cc. of hydrochloric acid (density = 1.12) into the tube (t) and introduce it into the flask, which is then stoppered. By opening the pinch-cock (r), and if necessary raising or lowering the levelling tube, bring the water level to the zero mark in the burette and see that the water in the levelling tube is exactly level with it. Tilt the decomposition flask so that the acid and the sample are mixed. As the water level in the burette falls, lower the levelling tube so that the two levels remain the same. When the decomposition is complete stand the reaction flask in a vessel full of water at laboratory temperature. After about three minutes adjust the water levels and read off the gas volume. It is necessary to correct the volume of carbon dioxide evolved by allowing for the carbon dioxide which has been absorbed by the hydrochloric acid used. The correction is made from Table I.

TABLE I.

Evolved ..	100.00	105.00	110.00	115.00	120.00	125.00	130.00	135.00	140.00	145.00	150.00
Absorbed ..	6.04	6.11	6.18	6.25	6.32	6.39	6.46	6.53	6.60	6.67	6.74
Evolved ..	155.00	160.00	165.00	170.00	175.00	180.00	185.00	190.00	195.00	200.00	—
Absorbed ..	6.84	6.88	6.95	7.02	7.09	7.16	7.23	7.30	7.37	7.44	—

*Example.*—Temperature = 15 deg. C. Barometric pressure = 764 mm. From Table II the weight of the sample = 0.8376 gram. Gas evolved = 145 cc. Correction for carbon dioxide absorbed by HCl = 6.67 cc. Total carbon dioxide = 151.67 cc.

$$\text{Per cent. of calcium carbonate} = \frac{151.67}{2} = 75.84.$$

**THE FAIJA CALCIMETER.**—Fig. 2 shows the Faija calcimeter: A is the generating bottle; C, gutta-percha acid tube; D, condenser with lead coil; E, gas-measuring tube having at its upper end two taps F and G; H, equilibrium tube, which may be moved up and down and secured in any position by fixing it on the rod I by means of thumb-screw K; L, barometer to which is attached the tap M; N, india-rubber ball attached by a tube to the barometer; this ball may be compressed or expanded by turning the handle O, thus adjusting the pressure in the instrument.

The instrument is first firmly secured to a wall with the tubes E and H vertical. The india-rubber tube P connects the lower ends of tubes E and H. Tube H

TABLE II.  
WEIGHT OF DRY GROUND SLURRY TO TAKE SO THAT 2 CC. OF CARBON DIOXIDE ARE EQUIVALENT TO  
1 PER CENT. CALCIUM CARBONATE.

Deg. C.	Barometric pressure.												760
	740	742	744	746	748	750	752	754	756	758	760		
10	0.8292	0.8316	0.8340	0.8360	0.8384	0.8406	0.8428	0.8452	0.8474	0.8496	0.8520		
11	0.8256	0.8280	0.8302	0.8324	0.8346	0.8370	0.8392	0.8414	0.8438	0.8460	0.8482		
12	0.8220	0.8242	0.8264	0.8288	0.8310	0.8332	0.8354	0.8378	0.8400	0.8422	0.8444		
13	0.8184	0.8206	0.8224	0.8250	0.8274	0.8296	0.8318	0.8340	0.8364	0.8386	0.8408		
14	0.8148	0.8170	0.8192	0.8214	0.8236	0.8260	0.8282	0.8304	0.8326	0.8350	0.8372		
15	0.8110	0.8132	0.8154	0.8176	0.8198	0.8220	0.8244	0.8266	0.8288	0.8310	0.8332		
16	0.8072	0.8094	0.8116	0.8138	0.8162	0.8184	0.8206	0.8228	0.8250	0.8272	0.8294		
17	0.8034	0.8056	0.8078	0.8100	0.8122	0.8144	0.8166	0.8188	0.8212	0.8234	0.8256		
18	0.7996	0.8018	0.8040	0.8062	0.8084	0.8106	0.8128	0.8150	0.8172	0.8194	0.8216		
19	0.7958	0.7980	0.8002	0.8024	0.8046	0.8068	0.8090	0.8112	0.8134	0.8156	0.8178		
20	0.7920	0.7942	0.7964	0.7986	0.8008	0.8030	0.8050	0.8072	0.8094	0.8116	0.8138		
21	0.7880	0.7902	0.7924	0.7946	0.7968	0.7990	0.8012	0.8034	0.8056	0.8078	0.8100		
22	0.7842	0.7864	0.7886	0.7906	0.7928	0.7950	0.7972	0.7994	0.8016	0.8038	0.8060		
23	0.7802	0.7824	0.7844	0.7866	0.7888	0.7910	0.7932	0.7954	0.7976	0.7996	0.8018		
24	0.7762	0.7782	0.7804	0.7826	0.7848	0.7870	0.7890	0.7912	0.7934	0.7956	0.7978		
25	0.7720	0.7742	0.7764	0.7786	0.7808	0.7828	0.7850	0.7872	0.7894	0.7916	0.7936		

Deg. C.	Barometric pressure.												780
	762	764	766	768	770	772	774	776	778	780			
10	0.8542	0.8564	0.8588	0.8610	0.8634	0.8657	0.8680	0.8702	0.8725	0.8748			
11	0.8506	0.8528	0.8550	0.8572	0.8596	0.8619	0.8642	0.8664	0.8687	0.8710			
12	0.8468	0.8490	0.8512	0.8534	0.8558	0.8581	0.8604	0.8626	0.8649	0.8672			
13	0.8430	0.8454	0.8476	0.8498	0.8520	0.8542	0.8565	0.8587	0.8610	0.8633			
14	0.8394	0.8416	0.8440	0.8462	0.8482	0.8504	0.8527	0.8549	0.8572	0.8594			
15	0.8354	0.8376	0.8400	0.8422	0.8444	0.8466	0.8489	0.8511	0.8534	0.8556			
16	0.8316	0.8338	0.8362	0.8384	0.8404	0.8427	0.8450	0.8472	0.8494	0.8516			
17	0.8278	0.8300	0.8322	0.8344	0.8365	0.8388	0.8410	0.8432	0.8455	0.8477			
18	0.8240	0.8262	0.8284	0.8306	0.8326	0.8348	0.8371	0.8393	0.8415	0.8437			
19	0.8200	0.8222	0.8244	0.8266	0.8287	0.8309	0.8331	0.8353	0.8376	0.8398			
20	0.8160	0.8182	0.8204	0.8226	0.8248	0.8270	0.8292	0.8314	0.8336	0.8358			
21	0.8122	0.8144	0.8164	0.8186	0.8207	0.8229	0.8251	0.8273	0.8295	0.8317			
22	0.8082	0.8104	0.8124	0.8146	0.8166	0.8188	0.8210	0.8232	0.8254	0.8276			
23	0.8040	0.8062	0.8084	0.8106	0.8126	0.8148	0.8169	0.8191	0.8212	0.8234			
24	0.7998	0.8020	0.8042	0.8064	0.8085	0.8107	0.8128	0.8150	0.8171	0.8193			
25	0.7958	0.7980	0.8002	0.8024	0.8044	0.8066	0.8087	0.8109	0.8130	0.8152			

A new instrument should be checked by the use of Iceland spar.

is then lowered until its upper neck is a little above the lowest reading on the tube E, a funnel is inserted in the neck H, and the tube filled with water until the water rises to the lowest reading in tube E. When filling the tube with water the taps F and G should be open and tube P pressed to expel any air. Distilled water is used, and in order that all air may be expelled it should be boiled and allowed to cool before it is poured into the instrument. The other india-rubber tubes are then attached, as shown in the drawing, the stopper is inserted into the generating bottle A, and taps G and M are closed. The instrument must be tight, and its tightness is ascertained by placing the equilibrium tube H in such

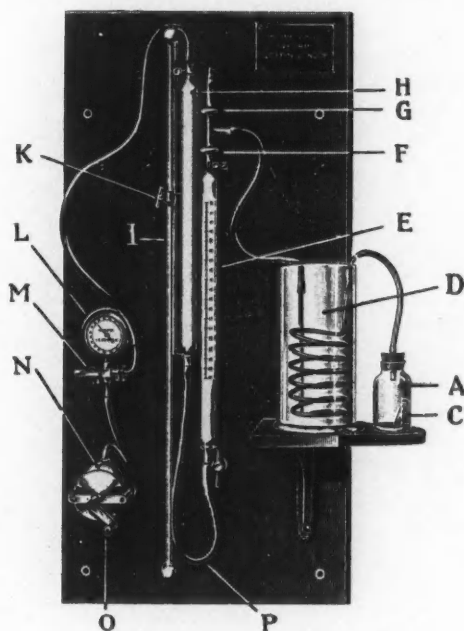


Fig. 2.

a position that there is a difference of several inches in the levels of the water in tubes E and H and noting the level of the water in tube E. If the instrument is tight the water will remain at this level for an indefinite period, but if the water in E rises or falls some of the joints are not tight and they must be bound with thin wire. The condenser D should be filled with water.

The mode of making the test is as follows. First remove the cork from the generating bottle A, take out the acid tube C, then open the taps F, G, and M. Elevate tube H to such a height that the water in tube E is exactly level with the mark immediately under tap F, and secure it there by turning the thumb-screw K. Weigh out 0.5 gramme of the dry ground slurry of which it is required

to ascertain the carbonate value, and place it in the generating bottle A. Run dilute hydrochloric acid into the tube C and wipe the outside; insert the tube with a pair of tongs into the generating bottle A. Tightly secure the stopper in the bottle A. Close tap G and slack the thumb-screw K, keeping tube H approximately in its elevated position. Now incline the bottle A so that the acid runs out of the tube C on to the slurry in A, and as the gas is generated lower tube H so as to keep the water in tubes E and H at approximately the same level. Continue shaking the bottle while the gas is generating, and be sure that all the acid has run out of the tube C. Place the generating bottle A in the water in the condenser D to cool the gas (which might have been heated by handling the bottle A) to the temperature of the water in the condenser D. Having left it there for a minute or so, remove the generating bottle and again shake it and note if any more gas is generated. When all the gas is generated (which is indicated by the water in tube E remaining in a constant position) close taps F and M, turn the handle O actuating the ball N in either one direction or the other so that the pressure in the barometer is diminished or increased until it indicates the normal pressure of 29.92 in. or 760 mm., which is more distinctly shown by the heavy line. Adjust tube H so that the water in it is exactly level with the water in tube E, and take the reading of the level of the water in tube E. This reading is the amount of gas developed at the standard pressure and only requires correction for temperature, which may be ascertained by tables as described later. When using the instrument the thermometer should be placed in and left in the water in the condensing vessel D. It is as well to try to adjust the temperature of the water to approximately the temperature of the room in which the apparatus is worked.

The essential portion of the Faija apparatus is the barometer added to the equilibrium tube, the pressure in which, and in the gas-generating tube, may be adjusted to a standard pressure of 760 mm. By this arrangement temperature is the only factor which it is necessary to consider when the volume of the gas has been ascertained by the reading of the instrument. The Faija apparatus has also the advantage of using a fixed weight of slurry. The instrument is first calibrated by Iceland spar at various temperatures and 760 mm. pressure; half a gramme is the weight used. In later experiments half a gramme of slurry is always used and the determination is always made at 760 mm. pressure. Thus suppose half a gramme of Iceland spar at 15 deg. C. gave  $x$  cc. of gas. Then at 15 deg. C., 1 cc. on the Faija apparatus =  $\frac{100}{x}$  per cent. of calcium carbonate. A table can now be drawn up as follows:

FAIJA CALIBRATION TABLE. PERCENTAGE OF CALCIUM CARBONATE IN DRY SLURRY. (Use 0.5 gr. sample and test at 760 mm. adjusted pressure.)

Temperature = 15 deg. C.

Gas evolved (cc.)	Per cent. calcium carbonate.
1.0	$100/x$
1.2	$1.2 (100/x)$

The table is now supplemented by determinations on Iceland spar at different temperatures so that a comprehensive table is easily made for all working temperatures.

**THE BAMBER CALCIMETER.**—The essential features of this apparatus are as follows: A decomposition bottle in which  $\frac{1}{2}$  gramme of slurry is placed together with a tube containing hydrochloric acid. The bottle can be immersed in a trough of water to maintain the contents at laboratory temperature, and is connected to a water-jacketed gas-measuring tube; the latter is connected to a levelling tube. A controlled water supply runs to the levelling tube so that the levels in the two tubes can be adjusted as required. The volume of gas evolved from the slurry at atmospheric pressure is determined, and the water jacket temperature is noted. The gas volume is then corrected to N.T.P. by the following method.

(1) **CORRECTION FOR ABSORPTION OF CARBON DIOXIDE BY ACID.**—The corrected calcimeter reading is obtained by adding to the observed reading in cubic centimetres a correction for absorption of carbon dioxide by acid. This correction may be obtained by a check estimate, using Iceland spar. The figure usually taken for this instrument lies between 3.5 and 4.2 cc.

(2) **DETERMINATION OF "CORRECTED" BAROMETRIC PRESSURE.**—Table III gives the deduction in millimetres of mercury to be made from the observed barometric pressure at the existing temperature.

TABLE III.

Temperature (deg. C.).	Aqueous vapour pressure (mm. mercury).	Temperature (deg. C.).	Aqueous vapour pressure (mm. mercury).	Temperature (deg. C.).	Aqueous vapour pressure (mm. mercury).
10.0	9.2	15.0	12.7	20.5	17.9
10.5	9.5	15.5	13.1	21.0	18.5
11.0	9.8	16.0	13.5	21.5	19.1
11.5	10.1	16.5	14.0	22.0	19.7
12.0	10.5	17.0	14.4	22.5	20.3
12.5	10.8	17.5	14.9	23.0	20.9
13.0	11.2	18.0	15.4	23.5	21.5
13.5	11.5	18.5	15.8	24.0	22.2
14.0	11.9	19.0	16.3	24.5	22.9
14.5	12.3	19.5	16.9	25.0	23.6
—	—	20.0	17.4	—	—

(3) **DETERMINATION OF CALCIMETER READING AT 0 DEG. C.**—Using Table IV under the observed temperature find the corrected calcimeter reading (or nearest) which was determined in para. (1); in a line with this is the calcimeter reading at 0 deg. C.

(4) Find the calcimeter reading at 0 deg. C. (from Table IV) under the corrected barometric pressure in Table V. In a horizontal line with this will be found the percentage of calcium carbonate at 0 deg. C. and 760 mm.

TABLE IV.  
CORRECTED CALCIUM READING AT DEG. C.

	0	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
80.0	82.92	83.11	83.52	83.82	84.10	84.30	84.69	84.99	85.30	85.60	85.99	86.30	86.60	86.80	86.98	87.30	87.60
80.2	83.12	83.32	83.72	84.02	84.31	84.51	84.89	85.19	85.50	85.80	86.19	86.50	86.80	86.98	87.18	87.50	87.81
80.4	83.33	83.52	83.92	84.23	84.51	84.71	85.09	85.40	85.70	86.00	86.40	86.70	87.00	87.21	87.50	87.81	88.01
80.6	83.53	83.72	84.12	84.43	84.71	84.91	85.29	85.60	85.90	86.20	86.60	86.90	87.21	87.50	87.81	88.11	88.41
80.8	83.73	83.92	84.33	84.63	84.91	85.11	85.50	85.80	86.10	86.40	86.80	87.10	87.41	87.70	88.00	88.31	88.61
81.0	83.93	84.12	84.53	84.83	85.11	85.31	85.70	86.01	86.31	86.61	87.00	87.31	87.61	87.91	88.21	88.51	88.81
81.2	84.13	84.33	84.73	85.03	85.32	85.52	85.90	86.21	86.51	86.81	87.21	87.51	87.81	88.11	88.41	88.72	89.02
81.4	84.34	84.54	84.94	85.24	85.53	85.73	86.11	86.41	86.71	87.01	87.41	87.71	88.01	88.31	88.60	88.92	89.22
81.6	84.54	84.74	85.14	85.44	85.73	85.93	86.31	86.61	86.91	87.21	87.61	87.91	88.21	88.51	88.80	89.12	89.42
81.8	84.74	84.94	85.34	85.64	85.93	86.13	86.51	86.81	87.11	87.41	87.81	88.11	88.41	88.71	89.00	89.32	89.62
82.0	84.94	85.14	85.54	85.84	86.13	86.33	86.71	87.01	87.31	87.61	88.01	88.31	88.61	88.91	89.21	89.52	89.82
82.2	85.14	85.34	85.74	86.04	86.33	86.53	86.91	87.21	87.51	87.81	88.21	88.51	88.81	89.11	89.41	89.72	90.02
82.4	85.34	85.54	85.94	86.24	86.53	86.73	87.11	87.41	87.71	88.01	88.41	88.71	89.01	89.31	89.61	89.92	90.22
82.6	85.54	85.74	86.14	86.44	86.73	86.93	87.31	87.61	87.91	88.21	88.61	88.91	89.21	89.51	89.81	90.13	90.43
82.8	85.74	85.94	86.34	86.64	86.93	87.13	87.51	87.81	88.11	88.41	88.81	89.11	89.41	89.71	90.01	90.33	90.63
83.0	85.94	86.14	86.54	86.84	87.13	87.33	87.71	88.01	88.31	88.61	89.01	89.31	89.61	89.91	90.22	90.53	90.84
83.2	86.15	86.35	86.75	87.05	87.34	87.54	87.91	88.21	88.51	88.81	89.21	89.51	89.81	90.11	90.42	90.74	91.04
83.4	86.35	86.55	86.95	87.25	87.54	87.74	88.11	88.41	88.71	89.01	89.41	89.71	90.01	90.31	90.62	90.94	91.24
83.6	86.55	86.75	87.15	87.45	87.74	87.94	88.31	88.61	88.91	89.21	89.61	89.91	90.21	90.51	90.82	91.14	91.44
83.8	86.76	86.96	87.36	87.66	87.95	88.15	88.52	88.82	89.12	89.42	89.72	90.02	90.32	90.63	90.94	91.26	91.56
84.0	86.96	87.16	87.56	87.86	88.15	88.35	88.72	89.02	89.32	89.62	90.04	90.34	90.63	90.94	91.25	91.57	91.87
84.2	87.16	87.36	87.76	88.06	88.35	88.55	88.92	89.22	89.52	89.82	90.14	90.44	90.73	91.04	91.35	91.67	91.97
84.4	87.37	87.57	87.96	88.27	88.55	88.75	89.12	89.44	89.74	90.04	90.34	90.64	90.93	91.25	91.56	91.88	92.18
84.6	87.57	87.77	88.17	88.47	88.75	88.95	89.32	89.64	89.94	90.25	90.54	90.84	91.13	91.45	91.76	92.08	92.38
84.8	87.77	87.97	88.37	88.67	88.95	89.15	89.52	89.84	90.14	90.45	90.74	91.04	91.33	91.65	91.96	92.28	92.58
85.0	87.97	88.17	88.57	88.87	89.15	89.35	89.72	90.04	90.34	90.65	90.94	91.24	91.53	91.85	92.16	92.48	92.78
85.2	88.17	88.37	88.77	89.07	89.35	89.55	89.92	90.24	90.54	90.85	91.15	91.44	91.74	92.05	92.36	92.67	92.97
85.4	88.38	88.58	88.97	89.28	89.56	89.76	90.13	90.45	90.75	91.06	91.36	91.65	91.95	92.25	92.55	92.86	93.16
85.6	88.58	88.77	89.17	89.48	89.76	89.96	90.33	90.65	90.95	91.26	91.56	91.85	92.14	92.44	92.74	93.05	93.35
85.8	88.78	88.97	89.38	89.68	89.96	90.16	90.53	90.85	91.15	91.46	91.76	92.05	92.34	92.64	92.94	93.25	93.55
86.0	88.98	89.17	89.58	89.88	90.16	90.37	90.73	91.05	91.36	91.66	91.96	92.25	92.55	92.85	93.15	93.46	93.76
86.2	89.18	89.38	89.78	90.08	90.37	90.57	90.94	91.26	91.56	91.86	92.16	92.46	92.75	93.05	93.35	93.66	93.96
86.4	89.38	89.58	89.98	90.28	90.57	90.77	91.14	91.44	91.74	92.04	92.34	92.64	92.94	93.24	93.54	93.85	94.15
86.6	89.58	89.78	90.18	90.48	90.77	90.97	91.34	91.64	91.94	92.24	92.54	92.84	93.14	93.44	93.74	94.05	94.35
86.8	89.79	89.99	90.39	90.69	90.98	91.18	91.54	91.84	92.14	92.44	92.74	93.04	93.34	93.64	93.94	94.25	94.55
87.0	89.99	90.19	90.59	90.89	91.18	91.38	91.74	92.04	92.34	92.64	92.94	93.24	93.54	93.84	94.15	94.46	94.76
87.2	90.19	90.39	90.79	91.09	91.38	91.58	91.95	92.25	92.55	92.85	93.15	93.45	93.75	94.05	94.36	94.67	94.97
87.4	90.40	90.60	90.99	91.30	91.48	91.78	92.08	92.38	92.68	92.98	93.28	93.58	93.88	94.18	94.49	94.79	95.09
87.6	90.60	90.79	91.19	91.50	91.68	91.98	92.28	92.58	92.88	93.18	93.48	93.78	94.08	94.38	94.68	94.98	95.28
87.8	90.80	90.99	91.40	91.70	91.88	92.18	92.48	92.78	93.08	93.38	93.68	93.98	94.28	94.58	94.88	95.18	95.48
88.0	91.00	91.19	91.60	91.90	92.08	92.38	92.68	92.98	93.28	93.58	93.88	94.18	94.48	94.78	95.08	95.38	95.68
88.2	91.20	91.40	91.80	92.10	92.28	92.58	92.88	93.18	93.48	93.78	94.08	94.38	94.68	94.98	95.28	95.58	95.88
88.4	91.40	91.60	92.00	92.30	92.48	92.78	93.08	93.38	93.68	93.98	94.28	94.58	94.88	95.18	95.48	95.78	96.08
88.6	91.60	91.80	92.20	92.50	92.69	92.99	93.29	93.59	93.89	94.19	94.49	94.79	95.09	95.39	95.69	95.99	96.29
88.8	91.81	92.00	92.41	92.71	92.90	93.19	93.49	93.79	94.09	94.39	94.69	94.99	95.29	95.59	95.89	96.19	96.49
89.0	92.01	92.20	92.61	92.91	93.10	93.40	93.70	94.00	94.30	94.60	94.90	95.20	95.50	95.80	96.10	96.40	96.70
89.2	92.21	92.41	92.81	93.11	93.30	93.60	93.90	94.20	94.50	94.80	95.10	95.40	95.70	96.00	96.30	96.60	96.90
89.4	92.41	92.61	93.01	93.31	93.50	93.80	94.10	94.40	94.70	95.00	95.30	95.60	95.90	96.20	96.50	96.80	97.10
89.6	92.61	92.81	93.21	93.51	93.70	94.00	94.30	94.60	94.90	95.20	95.50	95.80	96.10	96.40	96.70	97.00	97.30
89.8	92.81	93.01	93.41	93.71	93.90	94.20	94.50	94.80	95.10	95.40	95.70	96.00	96.30	96.60	96.90	97.20	97.50
90.0	93.02	93.21	93.62	93.92	94.10	94.40	94.70	95.00	95.30	95.60	95.90	96.20	96.50	96.80	97.10	97.40	97.70



TABLE V.  
CORRECTED BAROMETRIC PRESSURE.

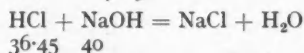
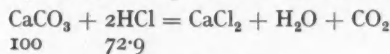
745	747	748	750	752	753	755	756	757	758	Per cent. CaCO <sub>3</sub> at 0 deg. C. and 760 mm.
84-21	84-01	83-87	83-62	83-46	83-32	83-14	83-05	82-91	82-78	74-00
84-49	84-29	84-15	83-90	83-74	83-60	83-42	83-33	83-19	83-06	74-25
84-77	84-57	84-43	84-19	84-02	83-88	83-70	83-61	83-47	83-36	74-50
85-05	84-85	84-71	84-47	84-30	84-16	83-98	83-89	83-75	83-62	74-75
85-32	85-12	84-98	84-75	84-57	84-43	84-26	84-16	84-02	83-89	75-00
85-65	85-40	85-26	85-03	84-85	84-71	84-54	84-44	84-30	84-17	75-25
85-93	85-68	85-54	85-31	85-13	84-99	84-82	84-72	84-58	84-45	75-50
86-20	85-96	85-82	85-59	85-41	85-27	85-10	85-00	84-86	84-73	75-75
86-49	86-24	86-10	85-87	85-69	85-55	85-38	85-28	85-14	85-01	76-00
86-76	86-52	86-38	86-15	85-97	85-83	85-66	85-56	85-42	85-29	76-25
87-05	86-80	86-66	86-43	86-25	86-11	85-94	85-84	85-70	85-57	76-50
87-32	87-08	86-94	86-71	86-53	86-39	86-22	86-12	85-98	85-85	76-75
87-61	87-36	87-22	86-99	86-81	86-67	86-50	86-40	86-26	86-13	77-00
87-89	87-64	87-50	87-27	87-09	86-95	86-78	86-68	86-54	86-41	77-25
88-17	87-92	87-78	87-55	87-37	87-23	87-06	86-96	86-82	86-69	77-50
88-46	88-20	88-06	87-83	87-65	87-51	87-34	87-24	87-10	86-97	77-75
88-73	88-48	88-34	88-11	87-93	87-79	87-62	87-52	87-38	87-25	78-00
89-02	88-76	88-62	88-39	88-21	88-07	87-90	87-80	87-66	87-53	78-25
89-30	89-04	88-90	88-67	88-49	88-35	88-18	88-08	87-94	87-81	78-50
89-59	89-32	89-18	88-95	88-77	88-63	88-46	88-36	88-22	88-09	78-75
89-87	89-60	89-46	89-23	89-05	88-91	88-74	88-64	88-50	88-37	79-00

760	762	763	765	766	767	768	770	771	772	775	Per cent. CaCO <sub>3</sub> at 0 deg. C. and 760 mm.
82-50	82-46	82-32	82-17	82-05	81-91	81-78	81-57	81-46	81-34	81-02	74-00
82-87	82-74	82-60	82-45	82-33	82-19	82-06	81-85	81-74	81-62	81-30	74-25
83-15	83-02	82-88	82-73	82-61	82-47	82-34	82-13	82-02	81-90	81-58	74-50
83-43	83-30	83-16	83-01	82-89	82-75	82-62	82-41	82-30	82-18	81-86	74-75
83-70	83-57	83-43	83-28	83-16	83-02	82-89	82-68	82-57	82-45	82-14	75-00
83-98	83-85	83-71	83-56	83-44	83-30	83-17	82-96	82-85	82-73	82-42	75-25
84-26	84-13	83-99	83-84	83-72	83-58	83-45	83-24	83-13	83-01	82-70	75-50
84-54	84-41	84-27	84-12	84-00	83-86	83-73	83-52	83-41	83-29	82-98	75-75
84-82	84-69	84-55	84-40	84-28	84-14	84-01	83-80	83-69	83-57	83-26	76-00
85-10	84-97	84-83	84-68	84-56	84-42	84-29	84-08	83-97	83-85	83-54	76-25
85-38	85-25	85-11	84-96	84-84	84-70	84-57	84-36	84-25	84-13	83-82	76-50
85-66	85-53	85-39	85-24	85-12	84-98	84-85	84-64	84-53	84-41	84-10	76-75
85-94	85-81	85-67	85-52	85-40	85-26	85-13	84-92	84-81	84-69	84-38	77-00
86-22	86-09	85-95	85-80	85-68	85-54	85-41	85-20	85-09	84-97	84-66	77-25
86-50	86-37	86-23	86-08	85-96	85-82	85-69	85-48	85-37	85-25	84-94	77-50
86-78	86-65	86-51	86-36	86-24	86-10	85-97	85-76	85-65	85-53	85-22	77-75
87-06	86-93	86-79	86-64	86-52	86-38	86-25	86-04	85-93	85-81	85-50	78-00
87-34	87-21	87-07	86-92	86-80	86-66	86-53	86-32	86-21	86-09	85-78	78-25
87-62	87-49	87-35	87-20	87-08	86-94	86-81	86-60	86-49	86-37	86-06	78-50
87-90	87-77	87-63	87-48	87-36	87-22	87-09	86-88	86-77	86-65	86-34	78-75
88-18	88-05	87-91	87-76	87-64	87-50	87-37	87-16	87-05	86-93	86-62	79-00

### The Acid-Alkali Method.

The acid-alkali process depends upon the decomposition of calcium carbonate by a measured quantity of standard acid in excess of that required by theory and then determining the excess acid by titration with standard alkali.



The solutions used are two-fifths of the normal. The indicator used is 1 per cent. phenolphthalein in 50 per cent. alcohol.

One cubic centimetre of hydrochloric acid (two-fifths normal solution) will decompose 0.02 gramme of calcium carbonate, and 1 cc. of two-fifths normal sodium hydroxide will neutralise this amount of acid. It follows that if a 1-gramme sample



is used for the determination then 1 cc. of standard alkali is equivalent to 2 per cent. calcium carbonate.

The method of determination is as follows. Weigh 1 gramme of the dried slurry (110 deg. C.) which has been ground to pass entirely through a 100-mesh sieve into a 300-cc. conical flask. Cover the powder with distilled water and then add slowly from a burette 50 cc. of two-fifths normal HCl. It is important that the acid should be added slowly in order to allow for drainage in the burette. Add 10 cc. of distilled water and boil for five minutes on a hot plate. Remove from the hot plate and rinse the sides of the flask with distilled water. Add two drops of phenolphthalein solution and titrate the liquid with two-fifths normal NaOH until the colour is pink. As the colour is often obscured the flask should be held to the light and the colour of the liquid observed as the solid matter settles. If the acid and alkali solutions are exactly equivalent and 1 gramme of the sample is used, Table VI enables the percentage of calcium carbonate to be read off at a glance.

TABLE VI.

Cc. alkali required.	Per cent. calcium carbonate.	C.c. alkali required.	Per cent. calcium carbonate.
10.5	79.0	11.9	76.2
10.6	78.8	12.0	76.0
10.7	78.6	12.1	75.8
10.8	78.4	12.2	75.6
10.9	78.2	12.3	75.4
11.0	78.0	12.4	75.2
11.1	77.8	12.5	75.0
11.2	77.6	12.6	74.8
11.3	77.4	12.7	74.6
11.4	77.2	12.8	74.4
11.5	77.0	12.9	74.2
11.6	76.8	13.0	74.0
11.7	76.6	13.1	73.8
11.8	76.4	13.2	73.6

#### The Correction of Slurry.

The following example from Meade's "Portland Cement" describes the method of correcting slurry. The general method is to mix together the contents of two or more tanks of slurry of known composition in such proportions that they will give a mixture of the desired composition. The data required are (1) Percentage of moisture in the slurry; (2) Percentage of calcium carbonate in the slurry; (3) Weight per cu. ft. of the slurry; (4) Dimensions of the slurry tanks.

To ascertain the weight per cubic foot of slurry, first weigh a litre flask empty, then weigh it filled with water, and again weigh it filled with slurry.

Let  $F$  = weight of flask filled with slurry,

$S$  = weight of flask empty,

$C$  = weight of flask filled with water.

$W$  = weight of one cubic foot of slurry in lb.

Then  $W = F - S / C - S \times 62.43$ .

An example is given in the following :—

	Mixer A	Mixer B
Moisture (per cent.) .. ..	38	40
Solids (per cent.) .. ..	62	60
Calcium carbonate (per cent.) .. ..	70.2	76.5
Weight per cb. ft. of slurry (lb.) ..	100.3	98.4
Diameter of tank (ft.) .. ..	25	25
Depth of slurry in tank (ft.) .. ..	15	16

A slurry of 74 per cent. calcium carbonate content is required. The dry slurries must be mixed in the following proportions :

$$A : B :: (76.5 - 74.0) : (74.0 - 70.2) :: 2.5 : 3.8.$$

$$\text{Solid matter in 1 cb. ft. of slurry (A)} = 100.3 \times 0.62 = 62.18 \text{ lb.}$$

$$\text{Solid matter in 1 cb. ft. of slurry (B)} = 98.4 \times 0.60 = 59.04 \text{ lb.}$$

The relative proportions by volume will then be

$$A : B :: \frac{250}{62.18} : \frac{380}{59.04} :: 4.02 : 6.44.$$

The volume of slurry (A) to be mixed with slurry (B) would then be found from the proportion  $A : B :: 4.02 : 6.44$ , or  $A = 10$  ft. to be mixed with 16 ft. of B. If the tanks differ in diameter or area of effective cross section the calculation must be based on cubic feet.

We are indebted to *Guide Pratique du Chimiste dans l'Industrie du Ciment*, by C. Tsountas, for Fig. 1, and to Messrs. Griffin & Tatlock, Ltd., for Fig. 2.

## The Coefficient of Expansion of Concrete made from Various Cements.

Experiments made by A. Guttmann, and described in *Zement* (p. 614, 1937), show that there are no important differences between the expansion coefficients of concretes made with a number of ordinary Portland cements in the region of ordinary temperatures when normal gravel is used and the cement content is about 300 kg. per cubic metre of concrete. It was also found that the expansion coefficient of old gravel concrete made with ordinary cement was about the same as that of steel and wrought iron, in this case 0.000012 and therefore higher than the value of 0.000010 which is accepted at present. Fresh gravel concrete has a still higher expansion. The author found a value of 0.0000156. By using an aggregate with a low expansion coefficient a reduction of the expansion to that of steel can be made.

## Design and Operation of Modern Lime Works.—X.\*

By N. V. S. KNIBBS, D.Sc.

### FUEL FOR LIME BURNING.

#### The Choice of Fuels.

PRACTICALLY all the known fuels are used for lime burning, but the low price of ordinary commercial lime makes it uneconomic to use the more costly fuels, such as town gas and charcoal. If there were no limit to the temperature which lime would withstand without damage, the fuel capable of generating the highest temperature would burn the largest amount of lime per unit of heating value; but the strictly limited temperature that is necessary in practice removes most of the difference between fuels other than those of low heating value, such as wood, lignite and blastfurnace gas.

The main factors governing the choice of a solid fuel for lime burning are (1) its ash content and the chemical composition and fusibility of the ash; (2) its content of volatile matter; (3) the reactivity of the non-volatile matter; (4) the chemical composition of the combustible and volatile constituents; and (5) its calorific value.

The ash in the fuel used in a mixed-feed kiln not only dilutes the fuel, but also influences its combustion inasmuch as a fuel with a low ash content is easier to burn completely than one with a high ash content. The ash also contaminates the lime and is mainly left mixed with the small lime, the impurity of which is therefore proportional to the ash content of the fuel. The large lime is also contaminated to an extent depending upon the method of charging the kiln, the temperature of the kiln, and the fusibility of the ash. The chemical composition of the ash mixed with or coated on the lime is important, since some impurities are more harmful than others in the uses to which lime is put. The ash of some fuels, for example, certain brown coals, consists largely of calcium oxide, and has very little influence on the purity of the lime.

In mixed-feed kilns of the simple type the combustible volatile matter in the fuel is lost, and it is important to use fuel with as low a volatile content as possible. In mixed-feed kilns specially designed for the combustion of the volatile matter, it is also important that this should not be too high because it is never completely burnt and because the efficient operation of these kilns depends upon a reasonably low ratio of volatile to non-volatile combustible matter.

The reactivity of the fuel and its relation to the efficiency of mixed-feed kilns has already been discussed<sup>1</sup>. It is of primary importance, but the lack of information makes it difficult to judge the suitability of a fuel except by trial. In a general way, however, it is known that metallurgical coke is less reactive than gas coke and gas coke less than coal, and that a low reactivity is necessary

\* Previous articles in this series appeared in our issues for January, February, March, April, May, August, September, October, November and December, 1937.

<sup>1</sup> *Cement and Lime Manufacture*, August, 1937, p. 211.

in a tall kiln working at high output per unit of cross-sectional area, and vice versa. Coke is therefore used in tall high-capacity kilns.

The chemical composition of the combustible and other volatile constituents of the fuel is important insofar as the constituents are liable to contaminate the lime produced. The most important contaminating impurity is sulphur, the effect of which has been discussed<sup>2</sup>. Chlorine is the only other common impurity. It is often present in small quantities in fuels and, being volatile, generally finds its way into the lime, but there is seldom enough to be important in any but a few of the chemical uses of lime.

The calorific value is a direct measure of the value of the fuel, and therefore does not require discussion, but the use of low-value fuels in mixed-feed kilns will be considered briefly. Low-grade fuels are seldom used in England and the United States, but are fairly widely used elsewhere. The quantity of low-grade fuel required for calcination is greater than that of a high-grade fuel, after allowing for the difference of calorific value, but fuels of low calorific value have the merit in mixed-feed burning of producing a lightly-burnt lime. This is because their rate of heat generation is low and the maximum temperature is correspondingly moderate. Where available at low cost they would therefore be excellent lime-burning fuels but for the fact that they are generally high in sulphur, which causes undue contamination of the lime. Nevertheless, they could probably be used more than they are at present.

The factors controlling the suitability of a fuel for gas-fired kilns are the same as those for mixed-feed kilns, but the importance of each may be quite different. Moreover, gas-kiln fuels include gases to which only factors 4 and 5 apply. Considering solid fuels which are gasified in a producer, the ash content matters only insofar as it affects the gasification of the fuel. As in its combustion, a high ash content entails a relatively high loss of combustible in the ashes. A high content of volatile material is an advantage in a fuel to be gasified, but if combined with caking properties it is undesirable because caking coal does not function well in a gas producer. A high reactivity of the non-volatile carbonaceous matter in the fuel is accompanied by a high rate of gasification in the producer and is therefore desirable. The chemical composition of the volatile matter has the same importance as in mixed-feed kilns.

In considering gaseous fuels, the important factors are the calorific value and the chemical composition insofar as the latter affects the purity of the lime and the rate of combustion of the gas, and therefore the length of the flame. Sulphur is usually the only impurity likely to be deleterious and many gaseous fuels are almost free from sulphur. Of the combustible constituents in gaseous fuels hydrogen tends to produce short flames and is therefore undesirable. Carbon monoxide and, still more, methane and other hydrocarbons produce flames favourable to lime burning.

In oil fuels sulphur is also the only impurity likely to contaminate the lime seriously, although some crude oils contain appreciable amounts of sodium

<sup>2</sup> *Cement & Lime Manufacture*, July, 1937, p. 197.

chloride. Although oil of low residual carbon content is preferable for lime burning, because it can be gasified by primary combustion to simulate more nearly a gas flame, practically any kind of oil may be used successfully.

The table gives the usual range of calorific values of most of the fuels used for lime burning, with the quantity of lime theoretically obtainable from them at 100 per cent. efficiency.

#### CALORIFIC VALUE OF FUELS.

Solid and Liquid (gross calorific values).

Fuel.	Calorific value per lb.		Lime : fuel ratio at 100 per cent. efficiency.
	B.Th.U.	C.H.U.	
Wood, dry <sup>3</sup> .. .. .	7,900-8,800	4,400-4,900	5.8-6.5
Coke <sup>4</sup> .. .. .	11,700-14,000	6,500-7,750	8.6-10.2
Anthracite <sup>5</sup> and steam coal .. .. .	12,600-14,900	7,000-8,300	9.2-10.9
Bituminous coal .. .. .	12,000-14,400	6,700-8,000	8.8-10.5
Lignite (dry) .. .. .	9,000-12,600	5,000-7,000	6.6-9.2
Peat (dry) .. .. .	8,100-10,800	4,500-6,000	5.9-7.9
Fuel oil <sup>6</sup> .. .. .	18,900-19,800	10,500-11,000	13.8-14.5

Gaseous (net calorific values, dry at 0 deg C.).

Gas.	Calorific value per cubic foot.		Tons of lime per 100,000 cubic feet of gas at 100 per cent. efficiency.
	B.Th.U.	C.H.U.	
Natural gas .. .. .	750-950	416-528	24.5-31.0
Coke-oven and town gas .. .. .	470-550	261-306	15.3-18.0
Blastfurnace gas .. .. .	85-115	47-64	2.8-3.8
Producer gas .. .. .	120-160 <sup>7</sup>	67-89 <sup>7</sup>	3.9-5.2

#### Wood.

Wood was the first fuel used for lime burning, but it is no longer in use on a large scale except in a few of the more recently settled countries and is rapidly being displaced even there. It is used either in some kind of flare kiln or in a continuous kiln with attached furnaces, and has the merit of burning with a long flame whose temperature never exceeds that at which practically all limes burn to a good soft-burnt product. It is also easily burnt, leaving very little ash, and it seldom, if ever, contains sufficient sulphur to contaminate the lime appreciably. Except for its high cost and low yield of lime, it is therefore almost an ideal fuel. Wood can be more efficiently used in modern plant embodying a semi-producer or producer, the gas being burnt in an ordinary gas-fired kiln. It is simple to gasify wood, and the high reactivity of the residual charcoal makes

<sup>3</sup> Wood as used generally contains between 25 per cent. and 45 per cent. of moisture.

<sup>4</sup> Not including petroleum coke.

<sup>5</sup> Not including high-ash anthracite duff and poor quality anthracites.

<sup>6</sup> Not including gas tar.

<sup>7</sup> The actual heating value of hot producer gas is higher than this by about 15-20 B.Th.U. (8-11 C.H.U.) owing to its sensible heat.

it unnecessary to use steam in the producer. Producers have been used to gasify wood waste but less frequently for logs, which are the more usual form of lime-kiln fuel. The only difficulty is in charging big pieces into the producer.

In China reeds are used as fuel, and in parts of Spain a kind of furze.

### Coke.

There are various types of coke available as lime-burning fuels, namely, beehive coke, horizontal retort coke, gasworks coke from horizontal and vertical retorts, and low-temperature coke. The efficiency attainable descends in the order named, which is the order of their reactivities, beehive coke having the lowest reactivity. It does not follow that the efficiency attained in all kilns would be highest with the least active coke. On the contrary, some short kilns with low output would burn very inefficiently with it, and much of the coke would pass through unburnt; but when kiln conditions are chosen to suit the fuel the least active gives the highest efficiency.

Coke is used in many of the kilns producing lime for metallurgical purposes, because they are generally situated in districts where metallurgical coke is obtainable at a low price. When the kilns are close to blastfurnaces, however, blastfurnace gas is generally available and is cheaper to use than coke. Consequently metallurgical coke is less used than formerly for burning lime for use in steelworks. It is used in nearly all kilns from which the exhaust gases are employed to supply carbon dioxide, but for burning for the ordinary market the larger producers generally find coal to be cheaper.

Gasworks coke is used if available locally at a reasonable price. It is less valuable for lime burning than metallurgical coke, not only because of its higher reactivity but also because its lower strength makes it more liable to be crushed in a tall kiln burning limestone. Low temperature coke is not used.

The size of coke is of considerable importance. Because the surface area exposed to the action of oxygen varies inversely as the size, small coke burns more rapidly than large, and therefore the size should be related to the time the lime-fuel mixture is in the burning zone. Coke in too large pieces is not completely burnt in the burning zone and descends into the cooling zone, where it either ceases to burn and is drawn with the lime or continues to burn and the carbon dioxide formed recarbonates the lime. A hard coke nearly always goes out. Of course, if there is a great deal of coke left unburnt at the bottom of the lime-burning zone there will be enough combustion to keep up the temperature, and the coke will continue to burn and the lime be overheated and spoiled.

The conditions to which a piece of coke is subjected in descending a kiln are somewhat complicated. As it descends it meets a current of hot gases depleted of oxygen and is heated to about 900 deg. C. when it arrives at the burning zone. While passing through this the coke is heated still more and, meeting oxygen-containing gases, begins to burn. As it descends through the burning zone, not only does its temperature increase up to a point at which loss of heat to the limestone and heat production by combustion balance, but it also meets a gas progressively richer in oxygen. The rate of combustion must therefore increase,



not only because of the increase of temperature but also because of the greater concentration of reacting oxygen. There comes a point at which the amount of combustible material left is insufficient to generate heat as quickly as it is used up, and the temperature begins to fall. If the coke is small the rate of combustion increases rapidly and the maximum is reached in a shorter distance than if it is large, so that the burning zone is shortened and intensified.

The velocity of the gases also comes into play as in an ordinary fire. A high velocity removes the products of combustion and supplies new oxygen, thus increasing the rate of burning enormously. Kilns with a high velocity of draught, having a high output per unit of cross-sectional area, therefore require coke in large pieces, and vice versa.

It has previously been pointed out<sup>a</sup> that the size of fuel in a mixed-feed kiln burning small lime should be correspondingly small, so that the heat generated may be uniformly distributed. It should also be small so as to generate heat rapidly, in accordance with the high rate of calcination of the small stone. Tall kilns, charged with 6-in. stone and operating at high output, use furnace coke of 3-in. size, and the most suitable sizes vary from that downwards.

#### **Anthracite and Steam Coal.**

Anthracite, and to a less extent steam coal, are widely used as lime-burning fuels when available at reasonable cost. They are used as run-of-mine coal, as slack, and as duff. Kilns operating on anthracite should be worked at a less output per unit of area than kilns burning coke, but they can also be shorter without detriment. The efficiencies obtainable are not as high as with coke, but it is easier to keep the fires alight when the kilns are damped down for week-ends or longer. Anthracite also makes a lightly burnt lime more easily than coke, owing to the possibility of burning it efficiently at lower temperatures. It is therefore suitable for use in kilns burning hydraulic and semi-hydraulic limes and dolomites, and is much used for the purpose.

There are many grades of anthracite. Since many are very low in ash and in sulphur, they produce a cleaner and purer lime than most other fuels that can be used in mixed-feed kilns.

The size of anthracite for lime-burning is governed by the same considerations as that of coke, but its higher reactivity makes the effect of size less pronounced. Very finely-divided anthracite (anthracite duff) is sometimes used for lime burning. Its use requires special care and it can be employed only in a kiln operating on low draught, otherwise the dust is carried out of the kiln with the current of gases. Also the kiln must contain stone of mixed sizes. If it is graded large stone, the dust falls through into the cooling zone immediately the charge is moved in drawing.

#### **Bituminous Coal.**

Bituminous coal is used to-day to burn the greater part of the lime made in England and the United States. In the latter country it is used in most of the very numerous furnace-fired kilns, in gas-fired vertical and rotary kilns

<sup>a</sup> *Cement and Lime Manufacture*, February, 1937, p. 61.



(other than those fired by natural gas), and in dust-fired rotaries. In England it is used in some of the largest mixed-feed plants and in most of the gas-fired plants. In the rest of Europe the majority of the mixed-feed kilns burn coke, but gas-fired kilns generally operate on a producer gas from a bituminous coal. Coal is also used on the grates of flare kilns.

Bituminous coal for use in a mixed-feed kiln specially adapted to use it<sup>9</sup> may be of almost any kind. A caking or semi-caking slack coal may be employed because the small coal cakes immediately it is fed in and thereafter acts as a lump, whilst the movement of the mass of limestone prevents it caking into too large a mass. On the other hand, combustion of the volatiles in these kilns is never very good, and when a high volatile fuel is used there is a copious evolution of black smoke. A low volatile fuel, such as may be used for steam raising on hand-stoked boilers, is therefore preferable.

Some kilns are fired with both bituminous coal and coke, the coke being fed in with the stone and the coal added lower down the shaft. A mixture of coal and coke has also been used in the simple type of mixed-feed kiln, but it is doubtful whether the results obtained have justified the use of the mixture.

Any of the non-caking bituminous coals may be used in producer-gas-fired kilns, subject to the factors already discussed.

Almost any kind of small coal, from slack to washed cobbles, may be gasified in producers of suitable design. A clean nut or cobble coal makes better quality gas at a higher rate of gasification and with less labour on the producer than a pea coal or slack, and the efficiency of gasification is higher. These factors must be taken into account in deciding which type is to be used on a producer-gas-fired plant. A slack or pea coal is generally very much the cheaper at the colliery, but since transport costs the same for each, the cost ratio in favour of the cheaper coal decreases with distance from the colliery and on remote plants it nearly always pays to buy a good quality nut coal of high calorific value.

For dust firing the same considerations apply as in cement making, but a coal low in ash and sulphur is desirable.

#### **Brown Coal, Lignite and Peat.**

Brown coal is used to a limited extent as fuel in ordinary mixed-feed kilns, but this is a most wasteful practice. The coal should be gasified, or used in a semi-gas producer, with or without briquetting. For successful gasification, some brown coal must be briquetted and in either form it generally requires a specially designed producer. Peat is best used in the same way.

In Australia there is a peat-like deposit (apparently formed from sea-weed) associated with a soft chalk-like calcium carbonate. The latter is too fine and soft to burn by itself; but the author found that it could be bound together by mixing with the peat, forming coherent lumps which were self-calcining. The

<sup>9</sup> *Cement and Lime Manufacture*, August, 1937, p. 214.

mixture, passed through a short shaft kiln, produced lime of good quality and the process was operated on a commercial scale.

### Shale.

Low-grade oil shales are used in some places to burn lime. In Sweden, for example, a Silurian hydraulic limestone occurs immediately above a shale of this kind, and the former is burnt in large chamber kilns with the shale and limestone inter-layered. There is considerable loss of volatile combustible matter, and a great weight of shale ash to dump, but the fuel is so cheap that the process is not uneconomical, and the low heating value of the shale prevents over-burning the lime.

Some shale residues from distillation of oil contain enough residual carbon to be used as lime burning fuels, but they are too poor to warrant the cost of transport and are therefore of local interest only. Shales of higher quality are best treated in a deep gas producer with or without recovery of oil, and the gas used in a gas-fired kiln.

### Oil.

Where it is available at a suitable price crude oil is an excellent fuel for a rotary kiln. It is less suited to shaft kilns on account of the difficulty of controlling the heat and attaining even distribution over the whole shaft. Moreover, natural gas is often available at a favourable price where oil is also available, and gas is always preferable. The use of oil is therefore confined to places where coal is expensive and oil relatively cheap, but where natural gas is not available.

Oil firing of vertical kilns has in the past been only moderately successful, due largely to poor application. Early oil-fired kilns embodied combustion chambers attached to the sides of the shafts, as it was considered that an empty chamber of this kind was necessary for successful combustion, but such an application of oil-firing must necessarily be inefficient, and modern kilns dispense with the combustion chambers and burn the oil, very finely atomised with just sufficient air to float it, amongst the lime. In other words, the conditions in a modern gas-fired kiln are duplicated as nearly as possible.

### Gas.

Of the various gases available as lime-burning fuels, natural gas is the most convenient to apply and the most efficient thermally, with coke-oven gas nearly its equal. Rich producer gas and the gas from a low temperature plant of the MacLaurin type, both cooled and cleaned, are also excellent fuels. Unfortunately none of these gases is ordinarily available in Europe for lime-burning, and the best gaseous fuel to be had is hot producer gas from a good quality coal. The use of this gas and of blastfurnace gas has already been discussed<sup>10</sup>.

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<sup>10</sup> *Cement and Lime Manufacture*, October, 1937, p. 277 et seq.

## Hydraulic Refractory Cements.

By SHOICHIRO NAGAI.

A SERIES of investigations is being undertaken by the author at the Institute of Silica Research of the Faculty of Engineering at the Imperial University of Tokyo, Japan.

Ordinary refractory materials of chamotte or silica origin are the most common and useful refractories, and are bound by refractory cement and mortars having nearly the same chemical compositions. These refractory cementing materials are made by mixing chamotte powder with a small amount of raw refractory clay powder. They have no or very poor hardening properties at room temperature when mixed with water, and bind refractory materials only when heated at high temperatures.

Poor hydraulic property is one of the most important disadvantages of this type of refractory cement, and the following notes describe some results of preliminary studies made with the object of preparing another type of hydraulic refractory cement.

It was considered that hydraulic refractory cement must comprise two or three important components, i.e., a refractory component, an hydraulic component, and a plastic component.

The refractory component was obtained from raw materials of diasporé or kyanite origins containing large amounts of alumina. These raw materials were first heated at higher temperatures than 1600 deg. C. in order to obtain stable chamotte which would not shrink or expand and then crushed to grains of suitable fineness. These raw materials of high alumina content were mixed with limestone and heated to form (a) calcium alumino-silicate  $x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{SiO}_2$  of low melting point and having hydraulic properties, as gehlenite  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , grossularite  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , etc., and (b) calcium aluminate  $x\text{CaO} \cdot y\text{Al}_2\text{O}_3$  of high alumina content, as  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$  or the mixed product of these aluminates. The heated product was ground to powder having hydraulic properties as calcium aluminate, or latent hydraulic properties introduced by mixing a small amount of lime as calcium alumino-silicate. As the third component slaked lime was used to increase the plasticity and introduce the latent hydraulic property of calcium alumino-silicate of the second component.

The hydraulic properties of the second components thus obtained were tested for (a) calcium alumino-silicate by mixing with slaked lime in the proportions of 80-85 : 20-15 and kneading with 65 to 70 per cent. of water, and (b) calcium aluminate without slaked lime by kneading with 35 to 40 per cent. of water and hardening for 3 and 7 days to test their compressive strengths.

The three components were mixed in the proportions of 85 to 95 parts of the first (refractory) powder of high-alumina chamotte, 12 to 5 parts of the second (hydraulic) powder of cement, and 3 to 0 parts of the third (plastic) component of slaked lime, and then kneaded with water (about 35 to 45 per cent.) and moulded in cylindrical pieces to test the compressive strengths at 7 and 28 days.

Five further samples of refractory cements were tested and compared with those already described.

A special method of chemical analysis was devised, which included systematic testing of various components soluble in water, in dilute acid solution, and then in dilute alkali solution. The water-soluble part was first separated by boiling the sample in water and analysed. The residue was then treated with a 5 per cent. solution of HCl on a water bath and the soluble part was separated and analysed. The second residue was then treated with a 10 per cent. solution of NaOH on a water bath and the chemical composition of the soluble part was tested. The residue from the alkali solution treatment was then analysed, and the water-soluble acid radicals such as  $\text{SO}_3$ , Cl, etc., were also tested by the first water-soluble solution. By this systematic treatment the soluble parts and the insoluble part were fully investigated.

The compressive strengths of cylindrical test pieces (20 mm. diameter by 30 mm. long) of refractory cements kneaded with water, dried, and burned at various temperatures (600, 800, 1000, 1200, 1300 deg. C., etc.), were tested, and it was observed that cements of low refractoriness had relatively large strengths when burnt at low temperatures (800-1200 deg. C.), whereas those of high refractoriness had smaller strengths at lower burning temperatures but large strengths if burnt at 1300 deg. C. or higher temperatures.

The test load (2 kg. per sq. cm.) during heating was applied on cylindrical test pieces (20 mm. in diameter by 30 mm. long). The expansion or contraction during heating was tested in accordance with the German standard for refractory materials (D.I.N. 1064, Druckerweichungsbestandigkeit), and the deformations after the test load were compared by the American standard for refractory materials (A.S.T.M. Standard Specification No. C16-20). These comparative tests clearly distinguished commercial refractory cements. Those of lower refractoriness showed considerably larger contraction and deformation even at relatively lower temperatures (1080-1200 deg. C.), and those of higher refractoriness showed smaller contraction and deformation even at temperatures above 1300 deg. C.

The author is now preparing experimental samples with high alumina contents, and the results of his tests will be reported in due course.

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